Modelling carbon formation using thermodynamic and kinetic methods in a steam methane reformer over nickel catalysts

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ABSTRACT

Steam methane reformers are used in industry to convert natural gas and steam into hydrogen, carbon dioxide and carbon monoxide. In order to operate a reformer efficiently and safely its behaviour needs to be understood. A numerical model has been developed in Python to replicate the reformer behaviour. The model considers reaction kinetics, pressure drop heat transfer and diffusion limitations within the catalysts. Data from industrial reformers will be used to regress model parameters.

Carbon can form on the catalyst surface at some operating conditions which can cause the catalyst to be less active and the whole reformer to run less efficiently. This process is known as coking. If the carbon is concentrated in one location in the reformer tubes a hot spot can develop which can be a safety concern. While some carbon can be removed with steam, the catalysts need to be replaced once there is too much carbon build-up. Carbon formation is predicted in the Python model using both thermodynamic and kinetic methods. The impact of catalyst deactivation will be replicated in the model to demonstrate the effect on reformer performance.

INTRODUCTION

Steam methane reformers are used in many industries to produce hydrogen and carbon monoxide. One of the challenges encountered with reformers is carbon formation on the nickel catalysts, known as coking. The carbon can block the pores on the catalyst which inhibits the catalyst activity. This clearly needs to be avoided by not operating the reformer at conditions that allow for coke formation.

Coke can be formed by either of the following reactions:

$$C_nH_m = nC + \frac{m}{2}H_2 \quad (1)$$

$$2CO = C + CO_2 \quad (2)$$

Hydrocarbon cracking by reaction (1) and Boudouard reaction (2) can lead to carbon forming on the catalyst surface.

A model has been developed in Python 3.4 to model the behaviour of a steam methane reformer (Holt, Kreusser, Herritsch, & Watson, 2018). Since that time, ethane, propane, butane and methanol have been added to the reaction scheme. Coking has been recently added and is explained in greater detail in the following sections.

Thermodynamics

The equilibrium constant can be calculated using the composition when the mixture is at equilibrium for the hydrocarbon decomposition and Boudouard reaction using the following equations:

$$K_h = \frac{p_{H_2}^{\frac{m}{2}} a_h^n}{p_{C_nH_m}} = \exp\left(-\frac{\Delta G_h^0}{RT}\right) \quad (3)$$

$$K_B = \frac{p_{CO_2} a_B}{p_{CO}^2} = \exp\left(-\frac{\Delta G_B^0}{RT}\right) \quad 4$$

If the equilibrium constant is known the equation can be rearranged to calculate the carbon activity

$$a_h = n\left(\frac{K_h p_{C_nH_m}}{p_{H_2}^{m\backslash 2}}\right)^{\frac{1}{n}} \quad 5$$

$$a_B = \frac{K_B p_{CO}^2}{p_{CO_2}} \quad 6$$

For pure substances, such as carbon, the activity is 1. Therefore if the activity is calculated to be >1, carbon is thermodynamically predicted.

The equilibrium constant of the carbon forming reactions can be calculated in a variety of ways. The Cantera (Goodwin, Speth, Moffat, & Weber, 2018) thermodynamics package can calculate the equilibrium composition of a gas mixture. Using equations 3 and 4 the equilibrium constant of all coking reactions can be calculated by assuming the activity of carbon is equal to 1.

The principle of equilibrated gas states that the gas should first be equilibrated then the coking tendency of that mixture can be calculated (Rostrup-Nielsen & Christiansen, 2011). The justification being that the gas will always be close to equilibrium in a steam methane reformer anyway. The possible limitation of this is that it does not take into account any hydrocarbons larger than methane. They are less stable and will not be present in the equilibrated mixture but their presence will make the mixture more prone to coking.

According to (Sperle, Chen, Lødeng, & Holmen, 2005) the overall thermal carbon activity from the degradation of all the hydrocarbons can be calculated:

$$a_C = \sum_i y_i a_{C_mH_m,i} \quad 7$$

where y_i is the hydrocarbon fraction

$$y_i = \frac{p_{C_nH_m}}{\sum_i p_{C_nH_m,i}} \quad 8$$

Alternatively the equilibrium constant can be calculated if the Gibbs free energy of a reaction is known. (Ginsburg, Piña, El Solh, & Lasa, 2005) provides a method for methane decomposition and Boudouard reaction:

$$\Delta G_{CH_4}^o = 58886.79 + 270.55 + 0.0311T^2 - (3.00 \times 10^{-6})T^3 + \frac{291405.7}{T} - 54.598T\ln(T) \quad 9$$

$$\Delta G_B^o = -188030.19 + 402.82 + 0.00524T^2 - (3.00 \times 10^{-6})T^3 + \frac{828509.9}{T} - 32.026T\ln(T) \quad 10$$

(Snoeck, Froment, & Fowles, 2002) and (Tavan, 2014) determined an expression for the threshold constant for methane cracking and the Boudouard reaction.

$$K^*_{CH_4} = \exp\left(\frac{154.1}{R}\right)\exp\left(-\frac{132830}{RT}\right) \quad 11$$

$$K^*_B = \exp\left(\frac{-170.44}{R}\right)\exp\left(\frac{162483}{RT}\right) \quad 12$$

Gasification of carbon on catalyst by carbon dioxide, hydrogen and steam need to be considered and also have their own threshold constants

$$K^*_{CO_2} = \exp\left(\frac{157.7}{R}\right)\exp\left(-\frac{148550}{RT}\right) \quad 13$$

$$K^*_H = \exp\left(\frac{-154.1}{R}\right)\exp\left(\frac{132830}{RT}\right) \quad 14$$

$$K^*_{H_2O} = \exp\left(\frac{136.7}{R}\right)\exp\left(-\frac{125916}{RT}\right) \quad 15$$

Kinetics

Carbon formation cannot be predicted by thermodynamics alone. Intermediates form so a kinetic model is needed to accurately predict carbon formation. Sometimes carbon will not be thermodynamically predicted but is kinetically predicted. (Rostrup-Nielsen J. , 1977)

When carbon forms it is adsorbed on the surface of the catalyst particle. These carbon atoms dissolve into the nickel, forming a selvedge with a high carbon concentration on the gas side. The carbon then diffuses through it to the support side. There, the carbon precipitates out and forms a filament. This filament will grow as the coking continues. The rate-limiting step of this process appears to be the diffusion of carbon through the nickel. Since no amount of coke formation is acceptable, accurately determining the rate of carbon formation is not necessary (Rostrup-Nielsen & Christiansen, 2011). Only an indication of whether there will be net carbon formation or gasification.

A reaction rate equation can be derived for this coking threshold, the conditions (temperature, concentrations etc.) where there is no coking or gasification (Snoeck, Froment, & Fowles, 2002) (Snoeck, Froment, & Fowles, 1997). At the threshold, there is no diffusion of carbon through the nickel particle and as the diffusion is the rate-limiting step, the concentration of carbon in nickel will be uniform across the particle.

$$r_{C,CH_4} = \frac{k^+_M \cdot K_{CH_4} \cdot p_{CH_4} - \frac{k^-_M{}'}{K_r{}''} \cdot p^2_{H_2}}{\left(1 + \frac{1}{K_r{}''} \cdot p^{\frac{3}{2}}_{H_2} + K_{CH_4} p_{CH_4}\right)^2} \quad 16$$

$$r_{C,B} = \frac{k^+_B K_{CO}\left(p_{CO} - \frac{1}{K^*_B}\frac{p_{CO_2}}{p_{CO}}\right)}{\left(1 + K_{CO}p_{CO} + \frac{1}{K_{O,CO_2}K_{CO}}\frac{p_{CO_2}}{p_{CO}}\right)^2} \quad 17$$

$$r_{g,CO_2} = \frac{\frac{k^+_O{}'}{K_{O,CO_2}}\left(\frac{p_{CO_2}}{p_{CO}} - \frac{1}{K^*_{CO_2}}p_{CO}\right)}{\left(1 + K_{CO}p_{CO} + \frac{1}{K_{O,CO_2}K_{CO}}\left(\frac{p_{CO_2}}{p_{CO}}\right)\right)^2} \quad 18$$

$$r_{g,H_2} = \frac{\frac{k_H^{+\prime}}{K_r''}\left(p_{H_2}^2 - \frac{1}{K_H^*}p_{CH_4}\right)}{\left(1 + \frac{1}{K_r''}p_{H_2}^{\frac{3}{2}} + K_{CH_4}p_{CH_4}\right)^2} \quad (19)$$

$$r_{g,H_2,H_2O} = \frac{\frac{k_H^{+\prime}}{K_r''}\left(p_{H_2}^2 - \frac{1}{K_H^*}p_{CH_4}\right) + \frac{k_O^{+\prime}}{K_{O,H_2O}}\left(\frac{p_{H_2O}}{p_{H_2}} - \frac{1}{K_{H_2O}^*}p_{CO}\right)}{\left(1 + \frac{1}{K_r''}p_{H_2}^{\frac{3}{2}} + K_{CH_4}p_{CH_4} + K_{CO}p_{CO} + \frac{1}{K_{O,H_2O}}\frac{p_{H_2O}}{p_{H_2}}\right)^2} \quad (20)$$

This set of equations is only valid where there is no coking or gasification due to the assumption of uniform carbon concentration in nickel. It can still be used as an indication of whether carbon will form or not.

RESULTS AND DISCUSSION

Various methods of calculating coking have been tested in Python 3.4 at a range of temperatures, hydrogen concentrations and steam/carbon ratios as these are the conditions that affect coke formation the most. The hydrogen concentration was varied in the natural gas with the composition shown in Table 1. Steam was added at a variety of steam/carbon ratios.

Table 1 Natural gas composition

Methane	82.02%	Isobutane	0.26%	Methanol	0.06%
Nitrogen	2.28%	Butane	0.25%	CO	0.03%
CO_2	5.50%	Isopentane	0.04%	Hydrogen	0.50%
Ethane	6.75%	Pentane	0.02%	Water	0.26%
Propane	2.02%	Hexane	0.01%		

The thermodynamic carbon activity from methane decomposition and the Boudouard reaction was calculated using equations 5 and 6 with Cantera used to calculate the equilibrium constant. The carbon activity was shown to be very dependent on temperature for methane degradation in Figure 1 and the Boudouard reaction in Figure 2. However, while carbon activity from methane degradation increases with temperature, it decreases with temperature for the Boudouard reaction. The hydrogen concentration only significantly affects the carbon activity from methane degradation since hydrogen is not involved in the Boudouard reaction. Carbon is predicted in all conditions tested except for low temperature and high hydrogen concentration. Figure 2 predicts carbon formation below ~670K with

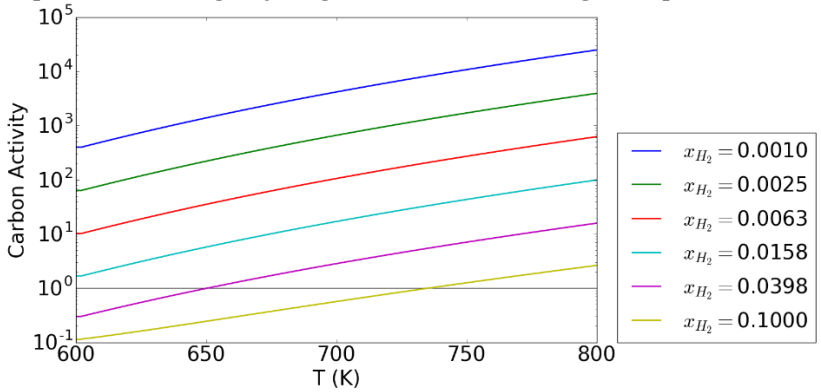

Figure 1 Comparing carbon activity at a range of hydrogen compositions. Calculated using Cantera equilibrium position from the methane decomposition mechanism.

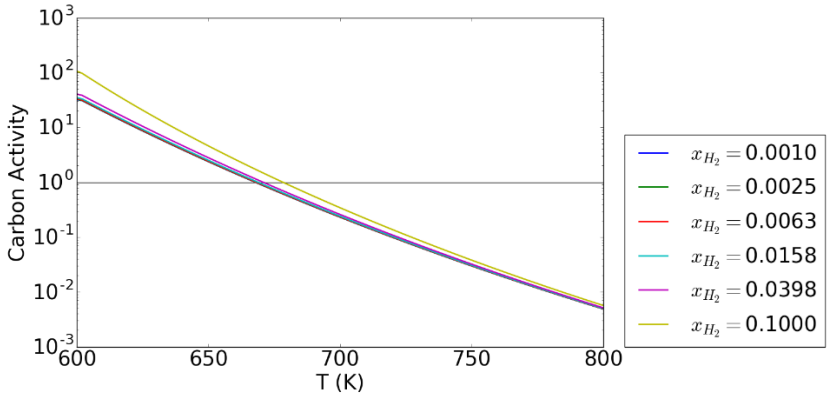

Figure 2 Comparing carbon activity at a range of hydrogen concentrations, calculated from the Boudouard mechanism using Cantera to calculate the equilibrium position.

the hydrogen concentration having little effect. This opposing behaviour indicates that both reactions need to be taken into account when predicting coke formation.

The method of calculating carbon activity has a significant impact on the calculated carbon activity as shown in Figure 3 and Figure 4. For the Boudouard reaction at a hydrogen mole fraction of 0.1%, only Cantera predicts any carbon formation. Snoeck and Ginsburg methods give carbon activities <1 for all the conditions tested. Figure 3 shows that all methods of calculating carbon activity from methane cracking predict carbon at low temperatures with a high hydrogen concentration however the critical temperature varies. The Sperle carbon activities were calculated using an equilibrium constant calculated using Cantera. Snoeck gives a similar critical temperature of ~750K but the Ginsburg critical temperature is significantly lower at ~680K. The Ginsburg and Snoeck methods only consider the relevant reaction when determining the equilibrium constant while the Cantera package will find the equilibrium position of the entire mixture with many possible reactions taken into account.

In Figure 7 it can be seen that the thermodynamic carbon activities for the hydrocarbon cracking increases with the hydrocarbon's molecular weight, showing that the higher hydrocarbons are more prone to coking than methane. The net carbon activity is between the methane and ethane carbon activities. Below ~740K carbon would not be predicted if only methane was considered but is predicted when these higher hydrocarbons are considered. It is therefore important to include the higher hydrocarbons as well as methane. This demonstrates the limitation of the principle of equilibrated gas, where the mixture is equilibrated before determining if it is prone to coking. Higher hydrocarbons are less stable than methane so are not present in an equilibrated mixture, such as one calculated by Cantera.

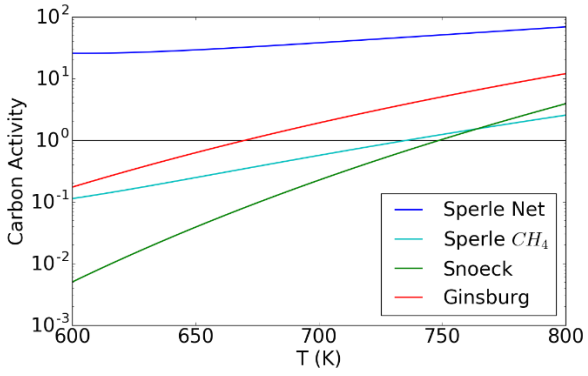

Figure 3 Comparing carbon activity calculated using a range of methods. Methane cracking mechanism

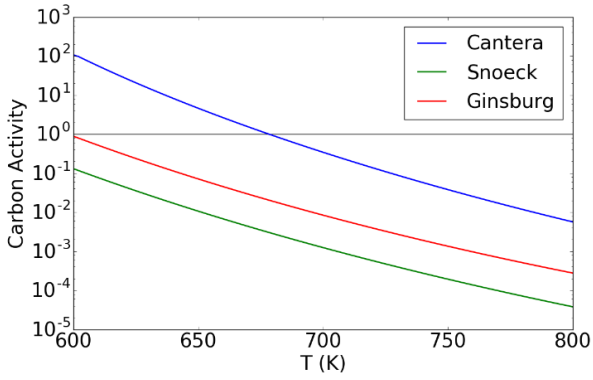

Figure 4 Comparing carbon activity calculated from Boudouard decomposition using 3 different methods

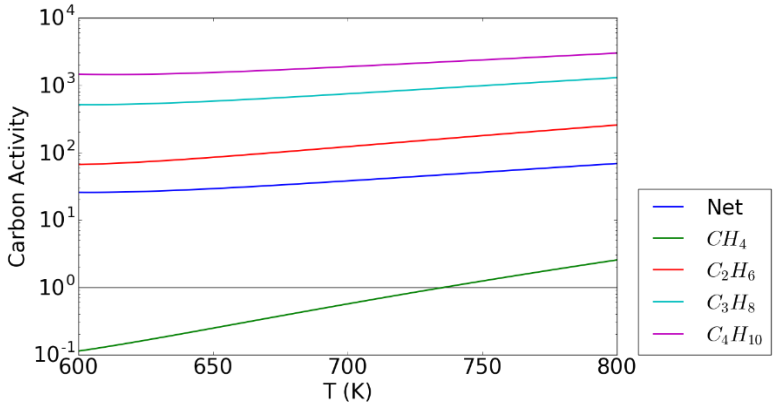

Figure 7 Carbon activity from the degradation of hydrocarbons using Sperle method and a hydrogen mole fraction of 10%.

The coking tendency of this equilibrated mixture would be much lower than the original mixture. Coking may not be predicted where it will occur.

When the steam/carbon ratio is altered, the carbon activity from methane decomposition changes as shown in Figure 5. A higher coking tendency is predicted with a higher steam/carbon ratio which does not reflect normal experience in industry. The difference is small however, compared to the effect of changing the hydrogen concentration alone. The Boudouard reaction is not affected significantly by the steam/carbon ratio as it does not involve hydrocarbons or steam.

Figure 8 and Figure 9 show that the rates of coking and gasification (Equations 16-20) depend heavily on temperature with rates of both gasification and coking increasing with temperature. There is a significant dependence on the hydrogen with there being net coking with a hydrogen fraction <1.6% and a net gasification with higher hydrogen concentration as shown in Figure 6. Methane cracking and carbon dioxide gasification are the biggest contributors to the net coking/gasification rate. The rate equations used here are valid only at the coking threshold (r=0) so the magnitude of the rates must be interpreted with caution.

The coking equations were tested on a simulation of a single tube in a steam methane reformer. While the heated section of tube is around 12m long, only the top of the reformer is shown in the following figures as coking is mainly observed there in industrial reformers. The carbon activity from the Boudouard reaction and methane decomposition calculated by Cantera are shown in Figure 10. Both mechanisms show dramatic change at the top of the tube since composition and temperature change

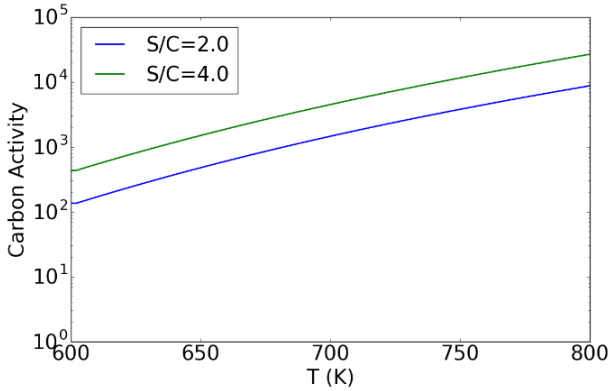

Figure 5 Comparing carbon activity calculated at a range of steam/carbon ratios. Using Cantera equilibrium function from the methane decomposition mechanism.

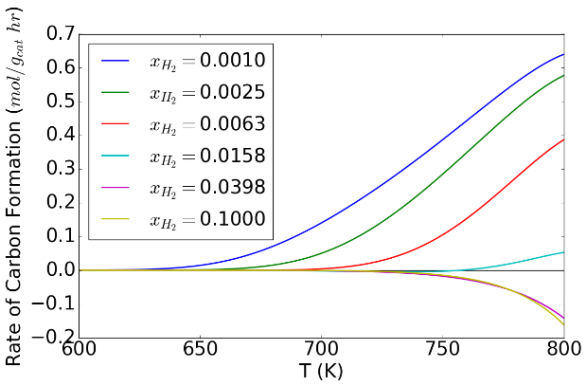

Figure 6 Net rate of carbon formation from Sperle method using a range of hydrogen concentrations with a steam/carbon ratio of 3.4.

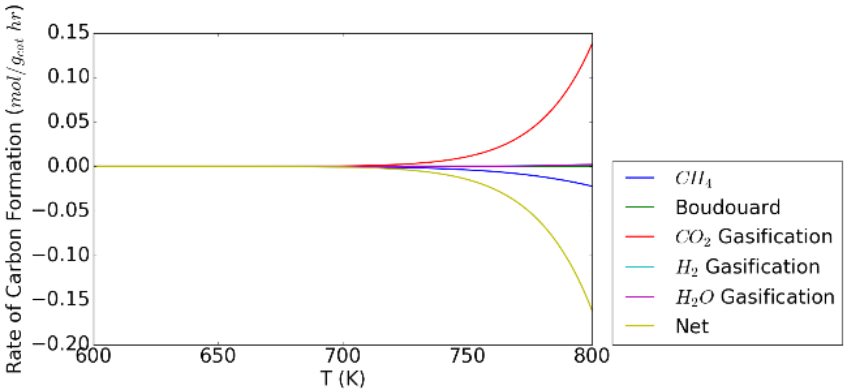

Figure 8 Rate of carbon formation and gasification with 10% hydrogen in the gas. Calculated using Snoeck method.

drastically. Boudouard activity increases while methane cracking decreases. At around 0.5 m they peak and the shift reverses as the temperature increases and the composition continues to change. The Boudouard carbon activity predicts carbon formation only in the top 1.5 m of tube. Methane cracking only predicts carbon formation after 1.5 m into the tube.

Figure 11 and Figure 12 show the net coking rates in the top 3.5 m of tube. The overall pattern of coking is not dependent on composition or temperature but the magnitude and location of coke does vary. Coking increases in the tube as the Boudouard reaction increases. It peaks at around 1-1.5 m into the tube when carbon dioxide gasification increases and dominates after 2-3.5 m and the net coking reverses and becomes net gasification. Steam content in the feed to the reformer reduces the coking. With lower steam/carbon ratios, the coking is located further down the tube. Temperature does not appear to affect the magnitude of coking but it does affect the location. Higher inlet temperatures cause coking to peak earlier in the tube. The distribution of coke formation reflects the thermodynamic carbon activity from the Boudouard reaction as this is the dominant reaction.

CONCLUSIONS

Models for carbon formation on catalysts in a steam methane reformer were studied in Python. All methods were tested at a range of temperatures and compositions. Thermodynamic based methods showed that methane cracking increases with temperature while Boudouard reactions are more prevalent at lower temperatures. Hydrogen significantly impacts the methane cracking with lower hydrogen concentrations favouring coking. The Boudouard reaction is not significantly affected by composition.

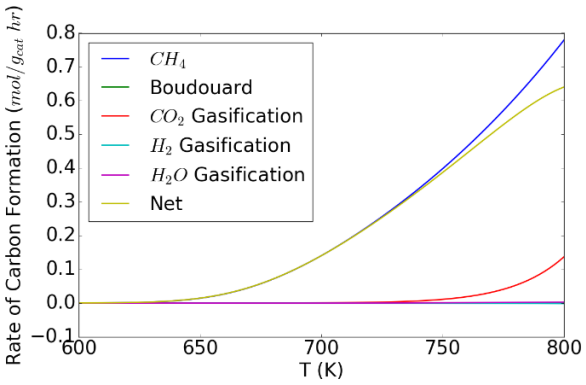

Figure 9 Rate of carbon formation and gasification with 0.1% hydrogen in the gas phase.

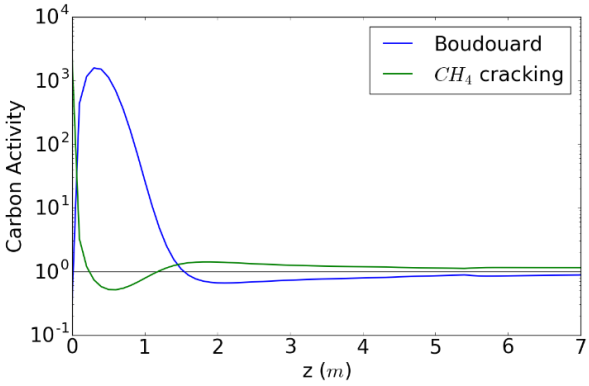

Figure 10 Comparing carbon activity from methane decomposition and Boudouard reaction using Cantera equilibrium concentrations.

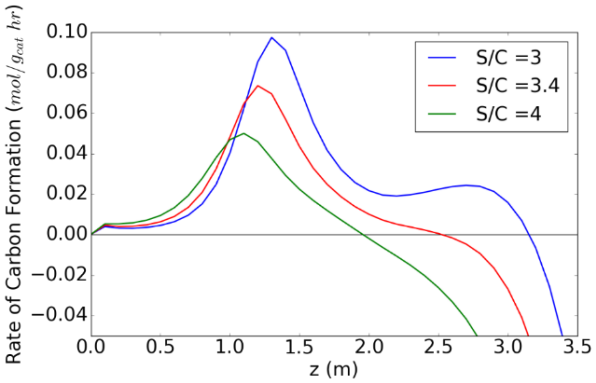

Figure 11 Comparing net coking rates in top of the reformer with a range of steam/carbon ratios. Inlet temperature of 350°C and hydrogen mole fraction of 3%.

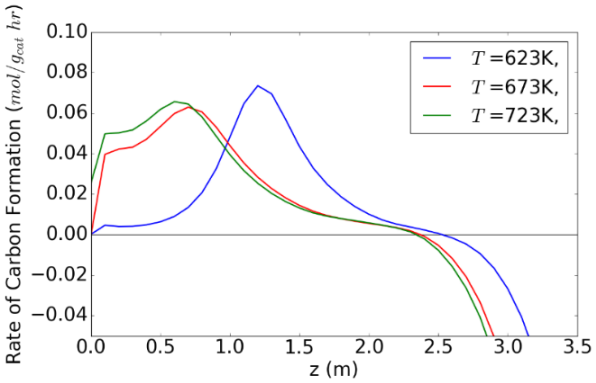

Figure 12 Net coking rates in the top of the reformer with a range of inlet temperatures. Steam/carbon ratio=3.4, H2 mole fraction=3%

While the Sperle and Cantera methods gave identical results for methane cracking, the other two gave significantly different carbon activities. The Sperle kinetic method reflected the dependence of coking on temperature and hydrogen concentration. In the reformer simulation, methane cracking and Bourdouard reactions gave very different patterns with Boudouard predicting carbon formation in the top 1.5 m of tube and methane cracking predicting coke further down. The kinetic method predicted coke formation to peak at about 1.5 m into the tube. Both the calculation of carbon activity from the Boudouard reaction and the Sperle kinetic method appear to be the most accurate indicators of carbon formation. Both these are based on Boudouard reaction.

NOMENCLATURE

a_x	Carbon activity calculated from reaction x	
$\Delta G_x°$	Gibbs free energy of reaction x	J/mol
k^+_B	Rate coefficients of the forward reaction of the rate determining steps of the Boudouard reaction	
k^+_H'	Rate coefficients of the forward reaction of the rate determining steps of gasification by hydrogen	
k^+_M, k_M-'	Rate coefficients of the forward and reverse reactions of the rate determining steps of methane cracking	
k^+_O'	Rate coefficients of the forward reaction of the rate determining steps of gasification by carbon dioxide	
K_i	Adsorption coefficient	
K_x	Equilibrium constant of reaction x	
K_x^*	Experimentally determined threshold constant of reaction x	
p_i	Partial pressure of component i	bar
R	Universal gas constant	J/mol K
$r_{c,x}$	Rate of coking by reaction x	mol/g_{cat}h
$R_{g,x}$	Rate of gasification by reaction x	mol/g_{cat}h
T	Temperature	K

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BIOGRAPHY

Jane Holt is a PhD student at the University of Canterbury in the Department of Chemical and Process Engineering. The topic of her research is creating a numerical model for a steam methane reformer, incorporating reaction kinetics, diffusion and temperature changes. The model is developed in Python, an open source programming language.

Dr Alfred Herritsch is the Senior Tutor for the first and second undergraduate year laboratories for the Department of Chemical and Process Engineering at the University of Canterbury. His research interest include process optimisation and mathematical modelling of various processes utilising Python, open-source programming language.

Associate Professor Matthew Watson teaches process design, numerical modelling, and energy-related courses in the Department of Chemical and Process Engineering at the University of Canterbury. He is a Fellow of the Institute of Chemical Engineers. His research areas include fossil fuel free extraction of metals, low energy alternatives to cement, and monolithic porous structures for adsorption and catalysis applications.